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TITLE NEW DEVELOPMENTS IN THE AB INITIO TREATMENT OF LOW-ENERGY ELECTRON COLLISIONS WITH MOLECULES

AUTHOR(S) B.I. Schneider
T.N. Rescigno
C.W. McCurdy
B.H. Lengsfield III

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

NEW DEVELOPMENTS IN THE AB INITIO TREATMENT OF LOW ENERGY ELECTRON COLLISIONS WITH MOLECULES

B. I. Schneider
Theoretical Division T–12
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

T. N. Rescigno
Lawrence Livermore National Laboratory
P. O. Box 808
Livermore, California 94550

C. William McCurdy
Department of Chemistry
The Ohio State University
Columbus, Ohio 43210

And
Byron H. Lengsfield III
Lawrence Livermore National Laboratory
P. O. Box 808
Livermore , California 94550

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Abstract

Although there has been substantial progress in the *ab initio* treatment of low energy electron scattering from small diatomic and polyatomic molecules in the last few years a number of problems still remain. Most current research has focused on the calculation of fixed nuclei scattering amplitudes in the static–exchange (SE) approximation. A few calculations have gone beyond this approximation to include electron correlation and/or vibrational and rotational effects, the latter often within the framework of model or parameterized potentials.

In this article we review a number of developments which have occurred since the last electron molecule satellite meeting at Daresbury Laboratory in July 1987. Our primary objective shall be to point out the strengths and weaknesses of current computational capabilities and to describe a new approach to electron polyatomic collisions using the complex Kohn method.

I. BRIEF HISTORY

The first *ab initio* calculations of electron molecule collisions were performed by Massey[1] and his collaborators in the 1950's using simple variational techniques. However, it is fair to say that it was only with the advent of high speed digital computers in the late 1960's and early 1970's that it became possible to integrate the close–coupling equations resulting from an expansion of the scattering wavefunction in Legendre polynomials[2]. This single center approach dominated the field for a number of years but it was clear that the difficulties of including the multi–center charge distribution, exchange and correlation within the existing formalism was formidable. In the ensuing decade a number of new techniques were developed which made substantial use of basis function expansions of the scattering wavefunction. The R–matrix[3] and T–matrix methods[4] were two of the earliest, general approaches which achieved success and were followed in rapid succession by hybrid techniques such as the Schwinger variational[5] and linear algebraic methods[6]. In these latter two theories there are components of numerical integration, analytic basis functions and physical grids. It is very curious in retrospect that the Kohn variational method[7], which was used quite successfully by Nesbet[8] in electron atom collisions, was never considered seriously in the molecular problem. Perhaps this was due to the presence of anomalous singularities in the K–matrices[8] which make the formalism difficult to apply in large scale calculations. In any event, by the early 1980's it was possible to perform static–exchange calculations on simple diatomic and linear polyatomic molecules[9] and a few calculations existed which included electron correlation using optical potentials or pseudostates[10].

In addition to these *ab initio* calculations there were numerous model exchange and polarization potential[11] calculations which were successful in reproducing a number of the features of *ab initio* theories with less effort. A few of these calculations went beyond the fixed nuclei approximation to include vibrational effects[12]. In most cases this was accomplished using a vibrational close coupling formalism, often with a local model potential, but a few calculations attempted to incorporate the true nuclear dynamics within a Born–Oppenheimer framework[13]. Early suggestions along these lines were made by Bardsley, Herzenberg and Mandl[14] using the Kapur–Peierls theory[15] and the Boomerang model[13a,b], so successful in expiaining the vibrational resonances in N_2, evolved from the formalism. In these latter approaches there is explicitly or implicitly recognized an internal region of configuration space where the nuclear and electronic motion can be adiabatically separated. The internal wavefunction is somehow matched or connected to the outside world using a frame transformation. A variant of this approach, within the R–matrix formalism, was developed by Schneider, Burke and LeDourneuf[13c] and applied

very successfully to resonant electron N_2 collisions[13d]. It has also been used in one form or another to treat the problem of threshold vibrational effects[13e,f] and may be valid for most vibrational excitation problems except very close to threshold.

In closing this historical section it is perhaps worth repeating that even today it is far from routine to perform a fixed nuclei scattering calculation on a first row diatomic molecule including correlation and/or many inelastic channels. Calculations such as these do exist but they are often expensive and uncertain in terms of convergence. In contrast, the calculation of highly accurate bound state wavefunctions for the low lying states of diatomic molecules is reasonably routine. This is a curious dichotomy considering the similarities of the two problems when the incident electron is within the molecular charge cloud. The molecular continuum wavefunction does not fall off exponentially at large distances as does the bound state wavefunction and is inherently more difficult to describe. An optimal approach would blend the power of the multi–center basis sets to describe the short range interactions with asymptotic functions to treat the long range multipole forces and to carry the scattering information to the outside world. A number of the theories mentioned earlier have this property but practical difficulties, which have only recently been overcome, have prevented applications to polyatomic systems. We explore these questions in more detail in the following sections.

II. Theory And Computation: The Problems

There currently exist a number of formal theories capable of treating the electron polyatomic scattering problem[4–6,9a]. All of these theories must deal with a number of fundamental questions. The need to account for correlation of the target electrons, correlation of the incident and bound electrons, nuclear motion, large or infinite numbers of open channels, ionization etc are independent of the formulation of the scattering problem. However, the manner in which we incorporate these into the calculation is highly dependent on the formalism. For example, the straightforward treatment of exchange requires the calculation of free–free and bound–free type integrals in a number of the theories mentioned above. Practical evaluation of these integrals for a polyatomic molecule is a highly non–trivial task. However the short range nature of exchange suggests that an L^2 expansion in terms of conventional basis sets should be adequate for computational purposes. Just how to integrate this into the particular formalism being used is the critical issue.

The major difficulties which must be addressed in developing an *ab initio* treatment of electron polyatomic collisions have some common and some distinct elements from the electron diatomic problem. As with the diatomics it is necessary to treat the electron correlations of both the target electrons and the correlation of the incident and target electrons. Here it is essential to develop a formalism capable of treating these effects in a balanced fashion. In almost all of the calculations performed on diatomic systems the targets have been treated at the single particle level and the incident–target correlation at the POLCI level[16]. Thus in a configuration interaction language the calculations have allowed single excitations from the SE reference configurations

of the elastic channel. This accounts quite well for the distortion of the ground state target orbitals from their unperturbed values and for long range polarization effects. If the ground and excited states need to be correlated and/or a more sophisticated treatment of incident–target correlation effects are required the situation is much less clear. Calculations which have attempted to go beyond the POLCI level have had difficulty in balancing N and (N+1) electron correlation effects[10]. Some authors[17] have used many–body perturbation theory and Greens' function methods to alleviate these difficulties but a fully integrated treatment remains a topic for future investigation. For polyatomic molecules there are additional complications which arise from the lower symmetry and additional vibrational degrees of freedom of the target. Thus even at the SE level it is necessary to calculate matrix elements which cannot easily be reduced to one or two dimensional quadrature. When this is combined with the difficulties of exchange and correlation the result is a formidable computational problem requiring considerable ingenuity for its solution.

In order to address these problems it is imperative to develop a formalism which is capable of drawing on the extensive experience of computational quantum chemistry and adding the necessary features to make the scattering problem tractable. Two approaches have appeared in the literature which have made progress in dealing with these questions and both are based on well–known variational principles due respectively to Kohn[7] and Schwinger[18].

The Kohn method has recently been reformulated with complex boundary conditions[19–20] which avoids the anomalous singularities associated with earlier work using the theory. In addition, the problems associated with exchange and correlation have been cast in a matrix optical potential language which is capable of drawing from the experience and computer codes of quantum chemists[21]. Adaptive quadrature schemes[22] in three dimensions have been developed which are capable of avoiding the slowly convergent, single–center expansions of earlier approaches to produce accurate values of the direct and transition potentials needed for the non–exchange free–free and bound–free integrals.

The Schwinger[5] approach has used a similar philosophy of introducing a basis set and reducing the scattering problem to the calculation of integrals and the solution of linear algebraic equations. The Schwinger variational principle has the advantage that it is based on an integral equation formulation of the scattering problem which does not require oscillatory basis functions as part of the variational space. The price one pays for this is the need to compute some difficult integrals involving the potential and the free particle Greens' function. These integrals are calculable but considerably more expensive to perform than those of the Kohn method which are of the Hamiltonian variety common to many bound state computations.

Before closing this section it is worth while remarking that the R–matrix method is also capable of being extended to the polyatomic scattering problem in much the same fashion as the Kohn method. These two formulations have many common features and it is possible to utilize the ideas of separable exchange and optical potentials within an R–matrix approach. The calculation of the additional types of matrix elements involving the model potential,

R–matrix functions could easily be done using the adaptive quadratures developed for the Kohn method. If Gaussian basis sets are used for the L^2 part of the expansion, it is possible to perform the direct integrations analytically. Explorations along these lines are currently in progress with Dr Cliff Noble of Daresbury Laboratory in the UK.

III. THE COMPLEX KOHN METHOD FOR POLYATOMIC MOLECULES: FIXED NUCLEI THEORY

There have been a number of developments in the Kohn variational method over the past two years which have made it a practical computational scheme for the calculation of electron polyatomic molecule cross sections[20–22]. In this section we review these developments for the fixed nuclei scattering problem.

As stated earlier the major obstacle in the application of the Kohn variational method to electron molecule collisions was the existence of the so called anomalous singularities which made large scale applications of the method difficult computationally. These singularities in the K matrix make it tedious to extract the scattering information since it is impossible to predict in advance where they will occur energetically or their number. In fact the more sophisticated the calculation becomes in terms of the number of L^2 terms included in the expansion of the wavefunction the more the singularities plague the calculation. The cure for this disease was shown by Miller and Jansen op der Haar[19] and McCurdy, Rescigno and Schneider[20] to be a reformulation of the Kohn variational principle with complex boundary conditions. This was in fact suggested more than a decade earlier by Mito and Kamimura[23] in nuclear scattering problems. Thus instead of working with the K matrix we focus on the T or S matrix. The T matrix form may be directly related to the Kapur–Peierls formulation of R matrix theory which is known to be anomaly free.

Once the basic formalism is in place it is necessary to find practical techniques for the computation of the matrix elements needed in the theory. In addition to the usual bound–bound type matrix element a Kohn calculation requires the calculation of bound–free and free–free type integrals. These integrals consist of kinetic energy, nuclear attraction, electrostatic and exchange type terms. The first three of these may be reduced to three dimensional quadrature. This is a formidable but tractable problem to which we return in a moment. The most difficult integrals involve the exchange of the incident and target electrons. These integrals cannot be computed analytically or reduced to low order quadrature by any approach known to these authors. Rescigno and Schneider[21] demonstrated that it was possible to rigorously eliminate these terms from the Hamiltonian by using a separable expansion of the exchange kernel. The essence of the idea is quite simple; since exchange is a short range interaction it is always possible to expand the exchange kernel in a set of L^2 functions. If we orthogonalize the free functions to the complete set of one particle bound orbitals the vanishing of the overlap integral assures us that the bound–free and free–free exchange matrix elements will vanish. Since it always permissible to use such a set in the calculation as a consequence of the

invariance of the scattering wavefunction to the process of orthogonalization our reformulation is both rigorous and extremely useful. In fact it is fair to state that without the use of the separable expansion and the invariance property of the wavefunction the calculation of polyatomic collision cross sections would be at least an order of magnitude more costly in computer time. These ideas may be extended to the correlation terms in the Hamiltonian if one is prepared to accept an L^2 expansion of both direct and exchange type integrals coupling the free and bound spaces. It is more difficult to justify such an expansion due to the presence of direct terms in the required matrix elements. However experience has shown that it is indeed possible and practical to do such an expansion. The fact that these integrals involve three bound state orbitals suggests that such an expansion would be practical. The use of the separable expansion for the correlation terms reduces our computational effort considerably. These terms may be then be incorporated into the theory via a Feshbach optical potential[36] which may be computed using standard bound state electronic structure theory. The merits of this formulation are that it is possible to utilize large scale configuration interaction programs to calculate the solution to the linear equations,

$$(E - QHQ) QXP = QHP \qquad (1)$$

where P(Q) projects onto the open(closed) parts of function space. These linear equations may be solved by approaches which do not require the Hamiltonian matrix to be in central memory of the computer. In fact all that is required of these techniques is the multiplication of the Hamiltonian on a vector. These vectors are then orthonormalized and used to expand the solution of eq(1). The coefficients in the expansion are chosen by projection or least squares methods. In all cases of interest the sequence of vectors so generated converges to an accurate representation of the desired solution in far less than the size of the original matrix. Since the approach requires no modification of the original matrix it may be read from a peripheral device or generated "on the fly" if that can be done efficiently. This latter approach is known as direct CI[24] in the quantum chemical literature and is the technique of choice for expansions involving matrices of the order 10^4 or larger. Once the linear equations have been solved it is a simple matter to compute the optical potential as,

$$V_{opt} = PHQQXP \qquad (2)$$

The reduced set of equations which "live" in P space are generally of much smaller dimension since they need only describe the open channels and may be solved by standard gaussian elimination using packaged routines such as those available in LINPACK[25]. Having eliminated the major computational roadblock let us return to the calculation of the direct matrix elements by numerical quadrature. The matrix elements involving the kinetic energy operator are no more difficult than the free–free and bound–free overlap integrals since it is possible to analytically differentiate the free and bound one particle functions. The interaction of the incident electron with the bound electrons of the molecule requires the evaluation of the potential on the

quadrature grid and the integration of the resultant potential between two orbitals. This process may be carried out in two steps. To compute the direct and transition potentials on the quadrature grid requires the calculation of integrals of the form,

$$V(\vec{r}) = \int \rho(\vec{r},\vec{r}') / |\vec{r}-\vec{r}'| \, d\vec{r}' \qquad (3)$$

where ρ is a density or transition density matrix. For polyatomic molecules ρ may be expressed as a bilinear combination of gaussian type atomic orbitals and the integral performed analytically. The analytic evaluation requires computing a number of special functions n^2 times where n is the number of primitive atomic orbitals. This is a non–trivial part of the calculation but fortunately it is energy independent, vectorizable and need only be done once. Given the potentials it is a relatively simple matter to perform the additional three dimensional numerical quadrature over the free or bound orbitals to obtain the final matrix elements. A key feature in making this process efficient is the generation of an integration grid accurate enough to represent the coulomb singularities at the atomic nuclei. This is particularly important when there are a number of atomic nuclei distributed arbitrarily in physical space. The approach we have used to date[22] is based on transforming a grid which is separable in (r,θ,ϕ) into a grid which produces a new set of points which are dense and approximately spherically symmetric around each nucleus. The transformation is defined by the equation,

$$\vec{r}(\vec{q}) = \vec{q} - \sum (\vec{r} - \vec{R}_{nuc}) S_{nuc}(\vec{q}) \qquad (4)$$

where $S_{nuc}(\vec{q})$ is a strength function chosen to be a weighted gaussian which draws the points toward the nucleus. We are currently exploring other schemes[26] which integrate in local co–ordinate systems around each atom and in a center of mass system between the atoms. This latter approach has the advantage of exact spherical symmetry around the atomic sites and reduces to the proper co–ordinates at long distances. It is essential in using such a system to recognize the possibility of discontinuities across the surfaces separating the regions. The main advantage of the use of such grid generation schemes is that it should be possible to obtain accurate results with substantially fewer integration points.

Once the matrix elements have been calculated they are substituted into the Kohn variational expression for the T matrix.

$$[T] = T^{trial} - 2 \langle \Psi^{trial} | H - E | \Psi^{trial} \rangle \qquad (5)$$

The variation of eq(5) produces a set of linear equations which are solved for the unknown coefficients of the L^2 functions and the trial T matrix. The stationary value of the T matrix is found by substituting the trial T matrix and wavefunction back into eq(5). Since the details are a rather standard exercise

we omit them here for lack of space. One final remark before closing this section is that the stationary expression for the T matrix is often much better than the values obtained from the solution of the linear equations. In fact it is often the case that small basis sets give very reasonable values for the scattering parameters in the variationally corrected results and quite poor results in the uncorrected form. This is another example of the power of a variational expression with a unsophisticated trial function.

IV. BEYOND THE FIXED NUCLEI APPROXIMATION

The calculation of vibrational and rotational excitation cross sections requires some work beyond the fixed nuclei approximation. In most instances it is sufficient to use the differences in time scales of the electronic and nuclear motion to simply average the fixed nuclei results over the ro–vibrational wavefunction. This approximation (adiabatic nuclei approximation), first suggested by Chase[27], is valid as long as the incident electron moves in and out of the interaction region rapidly compared to a ro–vibrational period. Thus the adiabatic nuclei approximation will be valid away from thresholds and in the absence of resonant collisions. Near thresholds the electron is moving very slowly and it is questionable if one can employ such a separation. In resonant collisions the electron spends a large fraction of its time near the target electrons and it is necessary to account for this in the description of the collision process. It is important to note however that even if the incident electron is near the other electrons and nuclei this does not necessarily signal a complete breakdown of the Born–Oppenheimer approximation. It may just have to enter the calculation in a more subtle fashion.

Basically there are two approaches to the inclusion of nuclear motion which go beyond the fixed nuclei approximation. The first of these, the vibrational close coupling expansion[12], treats the full collision problem without any recognition of a separation of nuclear and electronic motions in any part of configuration space. The result of the expansion is a set of coupled equations for the channel wavefunctions which may be solved using techniques developed for the fixed nuclei case. The major disadvantage of this approach is the size of the set of coupled equations which now depend on the vibrational as well as the electronic quantum numbers. The second class of theories make use of the Born–Oppenheimer separation[13] to somehow simplify the equations. The boomerang model of Herzenberg is an example of such an approach. However the physical idea is independent of the particular mathematical formulation. The essential ingredient of all of these theories is to introduce either in configuration or function space a set of solutions of the complete, fixed nuclei Schroedinger equation. Although these wavefunctions are only solutions of the electronic Schroedinger equation, the electrons are not required to move in the field of the undistorted charge distribution of the target. In a resonance the incident electron remains in the strong interaction region long enough for the other electrons to adjust to its presence. The nuclei then move on a potential surface which may be quite different from that of the target electrons. However, this adjustment may be adiabatic if the electrons motion is sufficiently rapid compared to the nuclear motion in the molecular core. Often this is the case and a full non–adiabatic theory is not necessary. What is

necessary is that the collision process be dominated by the short range physics and a resonant complex be formed. This is quite similar to the case of true bound states of molecules where the validly of the Born–Oppenheimer approximation is the rule rather than the exception in most situations. In a collision problem the electron eventually escapes and it is necessary to join the short and long range forms of scattering wavefunction to get a complete solution. This can be done by a matching procedure at a physical boundary as in the R–matrix or eigenchannel methods or by coupling the internal and external solutions of the Schroedinger equation with the potential.

The latter approach may be easily formulated within the framework of the Kohn variational principle by choosing a trial function of the form,

$$\Psi(r,R) = \sum A (\Phi \chi_\nu f_\nu) + \sum \psi_q \theta_q \qquad (6)$$

where Φ is the electronic ground state of the target, χ_ν a vibrational state of the target, ψ_q an L^2 function of the electronic Hamiltonian and θ_q a vibrational wavefunction associated with the L^2 function. We exclude the possibility of electronic excitation here for notational simplicity only. The scattering functions f_ν are expanded as is usual in the Kohn method as a linear combination of free waves.

$$f_\nu^{\nu'}(r) = f_\nu^0(r)\,\delta_{\nu\nu'} + T_{\nu\nu'}\, h^+_{\nu'}(r) \qquad (7)$$

The L^2 electronic functions are chosen here as solutions of the full electronic Hamiltonian ignoring the nuclear motion; that is as Born–Oppenheimer states. This allows us to bring the full apparatus of quantum chemistry to bear on the problem. If the first summation were absent the θ_q vibrational wavefunctions would be a set of quantized levels just like those in a true bound state. The coupling of the nuclear and electronic motion causes these vibrational levels to acquire a lifetime and to produce structure in the scattering cross section. The extent to which this occurs depends on the lifetime of the electronic state compared to the time of a vibrational period in that state.

The variation of the Kohn expression for the trial function given in eq(6) results in the following set of coupled equations,

$$\sum (\delta_{\nu\nu'} E - H_{\nu\nu'}) T_{\nu'\nu_0} + \sum \langle \chi_\nu \mid H_{\nu q}(R) \mid \theta_q \rangle = V^{+0}_{\nu\nu_0} \qquad (8a)$$

$$(E - E_q(R) - T_R) \theta_q(R) + \sum H_{q\nu}(R)\,\chi_\nu(R)\,T_{\nu\nu_0} = V_{q\nu_0}(R)\,\chi_{\nu_0}(R) \qquad (8b)$$

where,

$$V^{+0}_{\nu\nu_0} = < A(\Phi\, h^{+}_{\nu})\, \chi_\nu \mid V \mid A(\Phi\, f^{0}_{\nu_0})\, \chi_{\nu_0} >$$

$$V_{q\nu}(R) = < \psi_q \mid V \mid A(\Phi\, f^{0}_{\nu}) >$$

$$H_{q\nu}(R) = < \psi_q \mid E - H \mid A(\Phi\, h^{+}_{\nu}) >$$

$$H_{\nu\nu'} = < A(\Phi h^{+}_{\nu})\, \chi_\nu \mid E - H \mid A(\Phi h^{+}_{\nu'})\, \chi_{\nu'} >$$

We may now formally solve eq(8b) and substitute the solution into eq(8a). This results in an effective equation for the desired T Matrix,

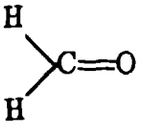
$$\sum (\delta_{\nu\nu'} E - H_{\nu\nu'})\, T_{\nu'\nu_0} - \sum < \chi_\nu \mid H_{\nu q}\, G_q\, H_{q\nu'} \mid \chi_{\nu'} >\, T_{\nu'\nu_0}$$
$$= V^{+0}_{\nu\nu_0} - \sum < \chi_\nu \mid H_{\nu q}\, G_q\, V_{q\nu_0} \mid \chi_{\nu_0} > \qquad (9)$$

We note that in this formulation, as in the R–matrix method, the electronic manifold of zeroth order states are coupled together via the vibrational Greens's function of the Born–Oppenheimer states. In general only one or two of these states will contribute in a resonant excitation and it is possible to simplify the equations considerably. The essential difficulty beyond the fixed nuclei approximation is the computation of the matrix elements involving continuum functions indexed by the label ν. . Approximations along the lines of the Boomerang model should simplify the calculation enormously.

In the final section we present some recent calculations using the complex Kohn formulation to electron formaldehyde (CH_2O) collisions in the fixed nucleus approximation. To our knowledge these are the first *ab initio* results on a polyatomic molecule including polarization in the elastic channel and to electronic excitation. The elastic scattering calculations show a pronounced resonance with vibrational structure quite similar to that in N_2 . These calculations are currently being extended to treat vibrational excitation using the formalism presented above.

V. RESULTS: ELECTRON CH_2O SCATTERING

CH_2O is a simple, yet non–trivial molecule to test the formal and computational scheme outlined in earlier sections. Its molecular structure is highly non–spherical



it contains both π and σ electrons and has a large permanent dipole moment. If one considers the molecular orbital structure of this molecule we would expect a low lying π^* (antibonding) orbital having a character quite similar to the π_g orbital in N_2. Thus the low energy scattering process should be dominated by a shape resonance of b_1 symmetry, the irreducible representation corresponding to π symmetry in the diatomic. The elastic scattering in the resonant symmetry was computed using an effective optical potential[28] of 624 configurations. The optical potential was constructed by generating all single excitations from the static exchange configurations which preserved the symmetry of the target and were singlet coupled. This is an excellent approximation for a shape resonant dominated collision in that it accurately reproduces the short range distortion of the target orbitals in the presence of the scattered electron. As has been stressed in N_2 this is not a polarizability effect but a distortion of the target orbitals which preserves symmetry. The effect of the optical potential is to lower the position of the resonance from its SE value and to place it in excellent agreement with available experimental data. The physical grid used to compute the bound–free and free–free matrix elements was constructed from an initial separable grid of 60,000 Gauss quadrature points and weights. As we have stated earlier we are in the process of exploring new approaches to the generation of physical grids which have the potential of reducing this number by an order of magnitude. Even with the present approach 60,000 points is a large "overkill" but we wanted to assure ourselves of convergence in this initial test problem. The long range dipole was treated using the MEAN method of Norcross and Padial[29] which allows us to present meaningful cross sections to compare against experiment.

The results are summarized in Figure 1. In the SE approximation the resonance appears at an energy nearly 2eV above the correct position with a far broader width than either the optical potential results or experiment. The results of the optical potential calculation place the position of the resonance essentially exactly at the experimental value. Our calculation, here performed only at the molecules equilibrium position, is somewhat narrower than the experimentally observed peak in the elastic channel. This is due to the need to include vibrational dependence in the collision process. Also shown in the figure is the cross section from the optical potential calculation at an angle of 120^0. The resonance peak is increasingly visible at larger angles where it is not obscured by the effect of the permanent dipole of the molecule.

Finally, we turn to some very preliminary results on the electronic excitation of CH_2O within a three state close coupling approximation[30]. The calculation included the lowest excited singlet and triplet states (A_2 symmetry) in addition to the ground electronic state. The orbitals for all of the states were computed using an average self consistent field approach in order to simplify the scattering calculation. This results in a poor description of the ground electronic state due to the lack of full double occupancy of the $2b_2$

orbital. The orthogonality constraints on the scattering functions of b_1 and b_2 symmetry are relaxed using a simple optical potential. The exclusion of such terms in a similar calculation of the excitation cross section in H_2 causes the results to be a factor of two too small. The cross sections were computed for the incident electron being in any one of the four possible spatial symmetries allowed by the point group of the molecule. The cross sections behave qualitatively as one would expect for singlet and triplet excitations. No experimental data is currently available so it is difficult to asses the accuracy of the results. Further calculations are underway to check the results and we expect to improve on the description of the target states and optical potential in the near future.

VI. CONCLUSION

The calculation of electron polyatomic collision cross sections from first principles is a challenging and computationally demanding task. We have described a new approach to the problem using the complex Kohn variational principle which has a number of important features, foremost of which is the rigorous elimination of free–free and bound–free exchange integrals and the need for single center expansions. The original fixed nucleus theory has been extended to include vibrational motion and some results for electron Formaldehyde scattering including correlation and electronic excitation have been presented. The future looks quite promising for applications to a wide variety of molecules and the extension to treat other processes such as molecular photoionization are already underway.

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30. Work In Progress

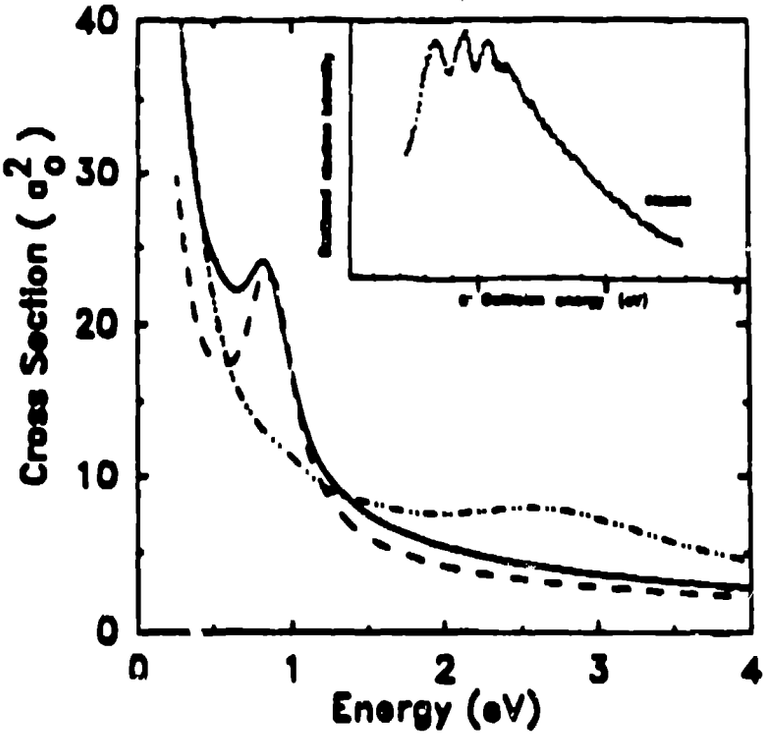

Figure 1. Elastic differential cross section for e^-–CH_2O. Solid curve: optical potential results at 90°; dashed curve: optical potential results at 120°; dashed–dot curve: static–exchange result at 90°. Insert shows experimental results of Benoit and Abouaf